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Metastable Phase Equilibria for the Quaternary System $Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K

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The isothermal evaporation method was employed to investigate the metastable phase equilibria in the quaternary system $Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K. The solubility and density of the metastable equilibrated solution were determined. The crystalloid forms of the solid phase were determined using chemical analysis and an X-ray diffraction method. On the basis of the experimental data, the metastable equilibrium phase diagram, water-content diagram, and density-composition diagram of the quaternary system were plotted. The phase diagram consists of three invariant points, seven univariant curves, and five crystallization fields corresponding to sodium borate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$), potassium borate tetrahydrate ($K_2B_4O_7 \cdot 4H_2O$), sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$), potassium carbonate sesquihydrate ($K_2CO_3 \cdot 3/2H_2O$), and a potassium and sodium carbonate double salt ($K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$). This quaternary system is of a complex type. $Na_2CO_3 \cdot 10H_2O$ is the only crystalloid form of sodium carbonate in the given system at 273.15 K. Sodium borate has the largest crystallization field and can be easily separated from the solution in this system at 273.15 K using an evaporation method. If borate needs to be separated as $K_2B_4O_7 \cdot 4H_2O$ as much as possible, a rise in temperature is necessary.

Introduction

Alkaline lakes are widely distributed in the area of the Qinghai-Xizhang (Tibet) Plateau. The Zabuye Salt Lake, located in Tibet, is one of the carbonate type salt lakes famous for its high concentrations of sodium, potassium, lithium, and borate as well as sulfate and carbonate ions.[1] The evaluated economic value of the Zabuye Salt Lake is more than 200 billion Chinese Yuan.[1] To economically exploit salt lake brine resources, it is important to adopt local natural energy such as the sun and wind, and thus a technique like the solar ponds is widely used. The technology of solar ponds is strongly dependent on the metastable equilibrium solubilities of salts, and therefore, investigation of metastable equilibrium is of important theoretical and practical significance.

The main components of Zabuye Salt Lake brine belong to the complex system $Li^+ + K^+ + Na^+ + B_4O_7^{2-} + CO_3^{2-} + Cl^- + SO_4^{2-} + H_2O$. By now, a series of papers describing metastable phase equilibria have been reported, such as papers about the seawater system $Na^+ + K^+ + Mg^{2+} + Cl^- + SO_4^{2-} + H_2O$ from (288 to 308) K,[2−5] as well as the system $Na^+ + K^+ + Cl^- + CO_3^{2-} + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 293 K.[6] However, most of the effort has focused on temperatures above 288 K, including our earlier work aimed at the Zabuye Salt Lake.[7,8] However, the climatic conditions in the Zabuye Salt Lake region are windy and arid, with high daily evaporation, and the average temperature is about 273 K.[1] Thus studies on phase equilibria at 273 K will be more closely related to reality and be of great use in the exploitation of the brine.

The quaternary system $Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ is an important subsystem of above-mentioned complex system of the Zabuye Salt Lake brine. No report has been found to describe the metastable phase equilibria of this system at 273.15 K. In this paper, the metastable phase equilibria of the aqueous system $Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ have been presented. The solubility and density of the equilibrated solution of this system were measured at 273.15 K.

Experimental Section

Reagents and Apparatus. The chemicals used in this work were of analytical purity grade and from either the Shanghai Chemical Reagent Plant or the Chengdu Chemical Reagent Plant. They were sodium borate [$Na_2B_4O_7$, 99.5 % (by mass)], potassium borate [$K_2B_4O_7$, 99.5 % (by mass)], sodium carbonate [Na_2CO_3, 99.0 % (by mass)], and potassium carbonate [K_2CO_3, 99.0 % (by mass)]. Doubly deionized water was obtained from a Millipore water system with an electrical conductivity less than $1 \cdot 10^{-4}\ S \cdot m^{-1}$ and pH = 6.6. For each experiment, the required amounts of reagents were dissolved in enough deionized water to produce the experimental solutions. The quantity of dissolved carbon dioxide from the atmosphere in the deionized water can be neglected during the analysis.

A SHH-250 type thermostatic evaporator made by the Chongqing INBORN Instrument Corporation, China, was used for the metastable phase equilibrium experiments. The temperature-controlling precision was ± 0.1 K.

Experimental Method. The isothermal evaporation method was employed in this study. According to the phase equilibrium composition, the appropriate quantity salts were dissolved into 1000 mL of deionized water as a series of artificial synthesized brines and loaded into clean opened polyethylene containers (24 cm long, 14 cm wide, and 7 cm high). The containers were placed in a thermostatic evaporator (SHH-250 type). The temperature of the solution inside the evaporator was controlled to (273.15 ± 0.1) K and measured by a Joule thermocouple with an operating range of (258.15 to 373.15) K and a system precision of ± 0.1 K. When enough new solid appeared in the evaporating containers, the liquid and solid phases were

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Table 1. Solubilities and Densities of Equilibrated Solutions in the Quaternary System $Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K[a]

	density	composition of equilibrated solution				Janecke index of dry salt					
no.	$g\cdot cm^{-3}$	$w(Na^+)$	$w(K^+)$	$w(B_4O_7^{2-})$	$w(CO_3^{2-})$	$J(Na_2^{2+})$	$J(K_2^{2+})$	$J(B_4O_7^{2-})$	$J(CO_3^{2-})$	$J(H_2O)$	solid phases
1, A	1.0821	3.12	0.00	0.82	3.75	100.0	0.00	7.80	92.20	7561	$Na_2CO_3\cdot 10H_2O + Na_2B_4O_7\cdot 10H_2O$
2	1.1029	3.38	0.84	0.93	4.69	87.25	12.75	7.12	92.88	5945	$Na_2CO_3\cdot 10H_2O + Na_2B_4O_7\cdot 10H_2O$
3	1.1078	3.41	1.46	1.22	5.10	79.88	20.12	8.46	91.54	5314	$Na_2CO_3\cdot 10H_2O + Na_2B_4O_7\cdot 10H_2O$
4	1.1272	3.42	1.70	1.06	5.36	77.33	22.67	7.09	92.91	5112	$Na_2CO_3\cdot 10H_2O + Na_2B_4O_7\cdot 10H_2O$
5	1.1308	3.21	2.38	1.16	5.57	69.60	30.40	7.48	92.52	4857	$Na_2CO_3\cdot 10H_2O + Na_2B_4O_7\cdot 10H_2O$
6	1.1699	3.72	3.67	1.10	7.24	63.25	36.75	5.53	94.47	3660	$Na_2CO_3\cdot 10H_2O + Na_2B_4O_7\cdot 10H_2O$
7	1.1938	3.55	5.69	1.17	8.54	51.44	48.56	5.02	94.98	2999	$Na_2CO_3\cdot 10H_2O + Na_2B_4O_7\cdot 10H_2O$
8	1.2279	3.61	6.41	1.25	9.14	48.89	51.11	5.01	94.99	2752	$Na_2CO_3\cdot 10H_2O + Na_2B_4O_7\cdot 10H_2O$
9	1.2521	2.14	15.71	0.93	14.51	18.76	81.24	2.42	97.58	1495	$Na_2CO_3\cdot 10H_2O + Na_2B_4O_7\cdot 10H_2O$
10, F_1	1.2561	2.19	16.15	0.95	14.88	17.83	82.17	2.56	97.44	1436	$Na_2CO_3\cdot 10H_2O + Na_2B_4O_7\cdot 10H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
11, B	1.0797	0.87	1.41	5.75	0.00	51.19	48.81	100.0	0.00	13813	$Na_2B_4O_7\cdot 10H_2O + K_2B_4O_7\cdot 4H_2O$
12	1.0812	0.99	1.62	5.95	0.24	50.88	49.12	90.49	9.51	11980	$Na_2B_4O_7\cdot 10H_2O + K_2B_4O_7\cdot 4H_2O$
13	1.0893	1.22	1.92	6.12	0.70	51.75	48.25	77.07	22.93	9782	$Na_2B_4O_7\cdot 10H_2O + K_2B_4O_7\cdot 4H_2O$
14	1.0976	1.26	2.02	6.38	0.73	51.36	48.64	68.77	31.23	9342	$Na_2B_4O_7\cdot 10H_2O + K_2B_4O_7\cdot 4H_2O$
15	1.1034	2.00	3.58	7.87	2.33	48.73	51.27	56.65	43.35	5235	$Na_2B_4O_7\cdot 10H_2O + K_2B_4O_7\cdot 4H_2O$
16	1.1119	2.24	4.37	7.05	3.55	46.54	53.46	43.41	56.59	4392	$Na_2B_4O_7\cdot 10H_2O + K_2B_4O_7\cdot 4H_2O$
17	1.1131	2.13	4.47	6.94	3.53	44.76	55.24	43.18	56.82	4447	$Na_2B_4O_7\cdot 10H_2O + K_2B_4O_7\cdot 4H_2O$
18	1.1234	2.35	5.22	7.49	4.17	43.34	56.66	41.00	59.00	3802	$Na_2B_4O_7\cdot 10H_2O + K_2B_4O_7\cdot 4H_2O$
19	1.1280	2.03	5.41	7.02	4.09	39.02	60.98	39.93	60.07	3987	$Na_2B_4O_7\cdot 10H_2O + K_2B_4O_7\cdot 4H_2O$
20	1.1260	2.02	5.21	6.10	4.27	39.75	60.25	35.53	64.47	4135	$Na_2B_4O_7\cdot 10H_2O + K_2B_4O_7\cdot 4H_2O$
21	1.1111	1.60	5.47	4.52	4.54	33.26	66.74	27.77	72.23	4441	$Na_2B_4O_7\cdot 10H_2O + K_2B_4O_7\cdot 4H_2O$
22	1.1354	1.68	6.30	3.78	5.57	31.21	68.79	20.79	79.21	3916	$Na_2B_4O_7\cdot 10H_2O + K_2B_4O_7\cdot 4H_2O$
23	1.2734	1.03	7.71	2.61	6.27	18.49	81.51	13.88	86.12	2175	$Na_2B_4O_7\cdot 10H_2O + K_2B_4O_7\cdot 4H_2O$
24, F_2	1.4289	1.87	21.05	0.73	18.31	13.14	86.86	1.51	98.49	1038	$K_2B_4O_7\cdot 4H_2O + Na_2B_4O_7\cdot 10H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
25, C	1.5544	0.00	31.06	4.67	22.03	0.00	100.0	7.58	92.42	589.3	$K_2B_4O_7\cdot 4H_2O + K_2CO_3\cdot 3/2H_2O$
26	1.5545	0.16	30.00	3.22	22.04	0.90	99.10	5.35	94.65	638.2	$K_2B_4O_7\cdot 4H_2O + K_2CO_3\cdot 3/2H_2O$
27	1.5574	0.23	29.36	2.25	22.02	1.33	98.67	3.80	96.20	672.1	$K_2B_4O_7\cdot 4H_2O + K_2CO_3\cdot 3/2H_2O$
28	1.5574	0.43	29.28	1.64	22.45	2.43	97.57	2.75	97.25	667.1	$K_2B_4O_7\cdot 4H_2O + K_2CO_3\cdot 3/2H_2O$
29	1.5578	0.59	29.37	0.91	23.01	3.29	96.71	1.50	98.50	658.0	$K_2B_4O_7\cdot 4H_2O + K_2CO_3\cdot 3/2H_2O$
30	1.5570	0.54	28.95	0.69	22.71	3.09	96.91	1.16	98.84	683.5	$K_2B_4O_7\cdot 4H_2O + K_2CO_3\cdot 3/2H_2O$
31	1.5569	0.89	29.22	0.85	23.32	4.94	95.06	1.39	98.61	644.7	$K_2B_4O_7\cdot 4H_2O + K_2CO_3\cdot 3/2H_2O$
32, F_3	1.5578	1.11	28.53	0.60	23.10	6.18	93.82	0.99	99.01	664.8	$K_2B_4O_7\cdot 4H_2O + K_2CO_3\cdot 3/2H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
33	1.5321	0.52	26.66	0.58	20.90	3.19	96.81	1.07	98.93	807.8	$K_2B_4O_7\cdot 4H_2O + K_2CO_3\cdot 3/2H_2O$
34	1.4743	1.15	27.86	0.58	22.66	6.58	93.42	0.98	99.02	694.1	$K_2B_4O_7\cdot 4H_2O + K_2CO_3\cdot 3/2H_2O$
35	1.4045	1.77	20.81	0.68	18.02	12.65	87.35	1.43	98.57	1069	$Na_2B_4O_7\cdot 10H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
36	1.4244	1.85	20.91	0.88	18.11	13.08	86.92	1.85	98.15	1049	$Na_2B_4O_7\cdot 10H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
37	1.4252	1.86	20.91	0.74	18.18	13.13	86.87	1.55	98.45	1050	$Na_2B_4O_7\cdot 10H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
38	1.4248	1.87	20.25	0.93	17.62	13.59	86.41	2.00	98.00	1098	$Na_2B_4O_7\cdot 10H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
39	1.3317	1.99	17.78	0.88	15.93	15.94	84.06	2.07	97.93	1299	$Na_2B_4O_7\cdot 10H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
40	1.3691	3.10	17.61	0.94	17.19	23.03	76.97	2.08	97.92	1159	$Na_2CO_3\cdot 3/2H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
41	1.3879	3.36	17.27	0.79	17.37	24.82	75.18	1.72	98.28	1155	$Na_2CO_3\cdot 3/2H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
42	1.3917	3.59	17.09	0.74	17.54	26.26	73.74	1.60	98.40	1141	$Na_2CO_3\cdot 3/2H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
43	1.4098	4.04	17.98	0.68	18.85	27.62	72.38	1.37	98.63	1020	$Na_2CO_3\cdot 3/2H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
44	1.4156	4.41	17.54	0.45	19.07	29.89	70.11	0.90	99.10	1015	$Na_2CO_3\cdot 3/2H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
45, D	1.4223	4.63	17.07	0.00	19.14	31.55	68.45	0.00	100.0	1028	$Na_2CO_3\cdot 3/2H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
46, E	1.5361	1.39	26.37	0.00	22.05	8.21	91.79	0.00	100.0	757.1	$K_2CO_3\cdot 3/2H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
47	1.5137	1.55	24.90	0.12	21.13	9.55	90.45	0.21	99.79	823.3	$K_2CO_3\cdot 3/2H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
48	1.5040	1.45	24.87	0.21	20.94	9.04	90.96	0.39	99.61	832.9	$K_2CO_3\cdot 3/2H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
49	1.5224	1.49	24.78	0.37	20.86	9.29	90.71	0.68	99.32	833.1	$K_2CO_3\cdot 3/2H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
50	1.5067	1.49	25.00	0.47	20.99	9.21	90.79	0.85	99.15	819.4	$K_2CO_3\cdot 3/2H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
51	1.5041	1.51	25.33	0.49	21.26	9.21	90.79	0.89	99.11	798.8	$K_2CO_3\cdot 3/2H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
52	1.5116	1.43	25.26	0.59	21.07	8.80	91.20	1.07	98.93	808.5	$K_2CO_3\cdot 3/2H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
53	1.5044	1.50	25.11	0.04	21.21	9.20	90.80	1.07	98.93	817.0	$K_2B_4O_7\cdot 4H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
54	1.5083	1.67	25.51	0.04	21.74	10.03	89.97	1.07	98.93	780.4	$K_2B_4O_7\cdot 4H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$
55	1.5161	1.79	25.25	0.87	21.37	10.74	89.26	1.54	98.46	777.0	$K_2B_4O_7\cdot 4H_2O + K_2CO_3\cdot Na_2CO_3\cdot 12H_2O$

[a] Note: *w*(B) - mass fraction of B; *J*(B) - Janecke index of dry salt.

separated by filtration. The obtained wet crystals were divided into two parts. One was analyzed by a chemical method to obtain the composition of the salts. The other was dried at 273.15 K, pestled into a powder, and then analyzed by X-ray diffraction to determine the crystalloid form of the solid phase. A Siemens D500 X-ray diffractometer with Ni-filtered Cu Kα radiation was used. The operating conditions were 35 kV and 25 mA.

At the same time, a 5.0 mL sample of the clarified solution was taken from the liquid phase and diluted to a 50 mL final volume in a volumetric flask filled with deionized water to analyze the concentration of liquid-phase components. Another 5.0 mL sample of the clarified solution was taken to determine the density. The remainder of the solution was loaded back into the polyethylene containers, placed in the thermostatic evaporator, and continued to be evaporated to reach the next measuring point. The same procedure was repeated until the solution was fully evaporated.

The densities of solution were determined in this study and used for mass fraction calculation of liquid components. The specific gravity bottle method with a correction of air floating force was used. The correction equation for density, ρ ($g\cdot cm^{-3}$), is

$$\rho = \frac{m_1 + A}{m_2 + A}\cdot \rho_0 \qquad (1)$$

where $\rho_0 = 0.9982\ g\cdot cm^{-3}$, the density of distilled water at 293.15 K, m_1 is the mass of the gravity bottle filled with sample, and m_2 is the mass of the gravity bottle filled with distilled water. A is the correction value of the air floating force,

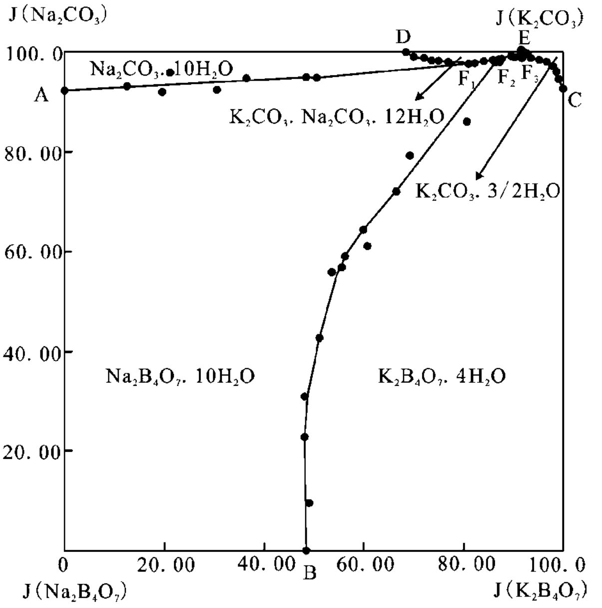


Figure 1. Metastable phase diagram of the quaternary system $Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K.

$$A = \rho_a \cdot \frac{m_2}{0.9970} \tag{2}$$

where $\rho_a = 0.0012\ g \cdot cm^{-3}$, the density of dry air at 293.15 K and normal atmospheric pressure.

The precision of the density measurements was 0.0001 $g \cdot cm^{-3}$. The sample was obtained at 273.15 K and measured at 293.15 K. The excursion caused by the temperature difference was calibrated by using a multipoint temperature revision method.[9]

Analytical Methods. The composition of potassium ion in the liquids and their corresponding wet solid phases was measured by a sodium tetraphenylborate (STPB)−hexadecyl trimethyl ammonium bromide (CTAB) titration [precision: ± 0.5 % (by mass)].[9] The sodium ion concentration was determined by inductively coupled plasma optical emission spectrometry [precision: less than 0.06 % (by mass), type ICP-OES 5300 V]. The carbonate ion concentration was determined by acid−base neutralization titration [precision: less than 0.5 % (by mass)].[10] The borate ion concentration was determined by neutralization titration in the presence of propanetriol [precision: ± 0.3 % (by mass)].[10]

Results and Discussion

Phase Diagram at 273.15 K. The experimental results of solubilities and densities of the equilibrated solution in the quaternary system $Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K are tabulated in Table 1. In Table 1, w(B) is the mass fraction of B, and J(B) is the Janëcke index value of B, with $J(Na_2^{2+}) + J(K_2^{2+}) = J(CO_3^{2-}) + J(B_4O_7^{2-}) = 100$ mol. With the data of the Janëcke index J(B), the experimental solubility isothermal metastable phase diagram of the system at 273.15 K is plotted in Figure 1. Figure 2 is the water-content diagram of this system.

The phase diagram of the quaternary system consists of five crystallization fields, three invariant points, and seven univariant curves. The five crystallization fields correspond to the single salt potassium borate tetrahydrate ($K_2B_4O_7 \cdot 4H_2O$), sodium borate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$), sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$), potassium carbonate sesquihydrate ($K_2CO_3 \cdot 3/2H_2O$), and dodecahydrated potassium and sodium carbonate double salt ($K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$). Salt $Na_2B_4O_7$ caused a salting-out effect on the salt Na_2CO_3. The crystallization field of the salt $K_2CO_3 \cdot 3/2H_2O$ is the smallest, while the crystallizing field of sodium borate is the largest. These results indicate that sodium borate is easier to saturate and crystallize than the other four salts from solution at 273.15 K.

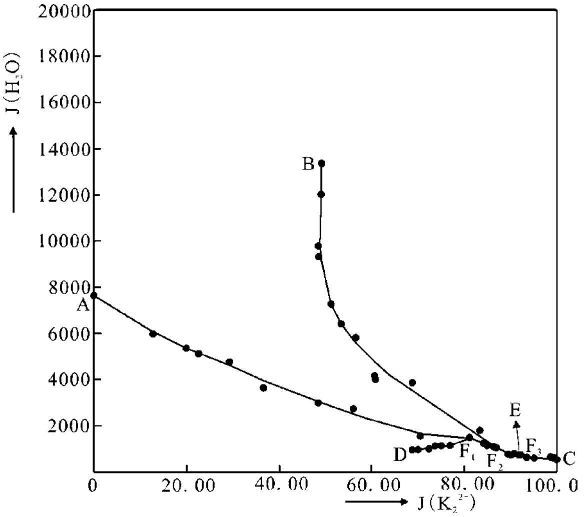


Figure 2. Water-content diagram of the quaternary system $Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K.

Three invariant points in this system are noted as F_1, F_2, and F_3, respectively. Points F_1 and F_3 are commensurate invariant points, while point F_2 is an incommensurate invariant point. The metastable equilibria solid phases in the invariant points were confirmed with X-ray diffraction analysis. Figure 3 gives the X-ray diffraction photograph of the invariant point F_1, which shows that, in the invariant point F_1, the salts $Na_2CO_3 \cdot 10H_2O$, $K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$ and $Na_2B_4O_7 \cdot 10H_2O$ exist. The saturated salts and the mass fraction composition for the three invariant points are listed below.

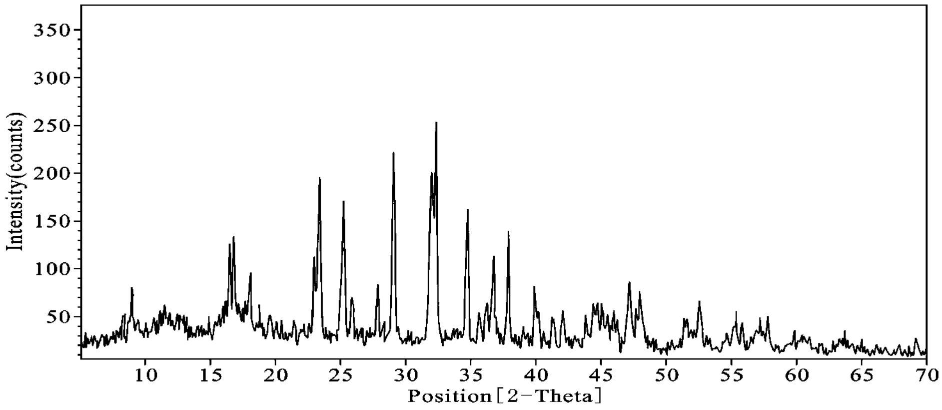
Point F_1 is saturated with salts $Na_2CO_3 \cdot 10H_2O + Na_2B_4O_7 \cdot 10H_2O + K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$. The mass fraction composition of the corresponding liquid phase is $w(Na^+) = 2.19$ %, $w(K^+) = 16.15$ %, $w(B_4O_7^{2-}) = 0.95$ %, and $w(CO_3^{2-}) = 14.88$ %.

Point F_2 is saturated with salts $Na_2B_4O_7 \cdot 10H_2O + K_2B_4O_7 \cdot 4H_2O + K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$. The mass fraction composition of the corresponding liquid phase is $w(Na^+) = 1.87$ %, $w(K^+) = 21.05$ %, $w(B_4O_7^{2-}) = 0.73$ %, and $w(CO_3^{2-}) = 18.31$ %.

Point F_3 is saturated with salts $K_2CO_3 \cdot 3/2H_2O + K_2B_4O_7 \cdot 4H_2O + K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$. The mass fraction composition of the corresponding liquid phase is $w(Na^+) = 1.11$ %, $w(K^+) = 28.53$ %, $w(B_4O_7^{2-}) = 0.60$ %, and $w(CO_3^{2-}) = 23.10$ %.

The seven isothermal evaporation curves in the system correspond to curves AF_1, BF_2, CF_3, DF_1, EF_3, F_1F_2, and F_2F_3, indicating the cosaturation of two salts. Points A, B, C, D, and E, cosaturated with two salts, are the invariant points of the four ternary subsystems of the quaternary system $Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$.

Figure 2 is the water-content diagram of the quaternary system. At the invariant point F_3, the system has the lowest water content. Invariant point F_3 is a congruent eutonic point and the evaporating end point of the whole system. At this point, the salts $K_2CO_3 \cdot 3/2H_2O$, $K_2B_4O_7 \cdot 4H_2O$, and $K_2CO_3 \cdot N_2CO_3 \cdot 12H_2O$ can be salted out simultaneously, without any dissolving conversion action.



Chemical Formula	$KNaCO_3 \cdot 6H_2O$	$Na_2CO_3 \cdot 10H_2O$	$Na_2B_4O_5(OH)_4(H_2O)_8$
Dspacing	2.77	3.08	2.58
Score	32	28	34

Figure 3. X-ray diffraction photograph of the invariant point F_1 ($Na_2CO_3 \cdot 10H_2O + Na_2B_4O_7 \cdot 10H_2O + K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$).

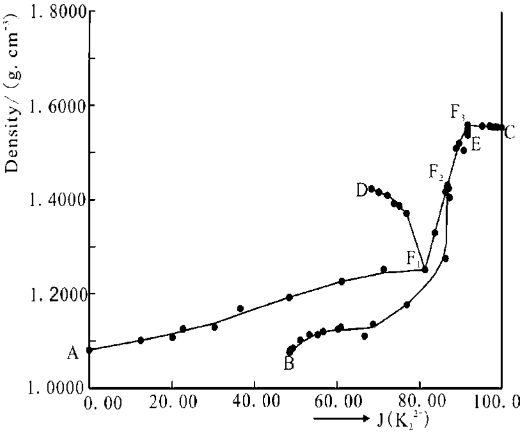


Figure 4. Density property vs K^+ composition diagram of the equilibrated solution in the quaternary system $Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K.

In the phase equilibrium of the quaternary system $Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K, the crystalloid form of potassium carbonate is $K_2CO_3 \cdot 3/2H_2O$, and because that of sodium carbonate is $Na_2CO_3 \cdot 10H_2O$, no $Na_2CO_3 \cdot 7H_2O$ or $Na_2CO_3 \cdot H_2O$ is formed. These results greatly agree with our earlier research results.[11]

The dissolving behavior of boron is very complicated in aqueous solution. Borates can form different polyanions in solution, and the various species of boron depend on the pH value, the total concentration of boron and salts, and the kinds of coexistent salts.[12] At a high concentration of boron, $[B_4O_5(OH)_4]^{2-}$ is the main species of boron, and $B_4O_7^{2-}$ is used as the traditional stoichiometry to express the various boron species in solution.[13] In this metastable equilibria, the equilibrium solid phases of sodium borate and potassium borate exist with tetraborate, with the structure formed as $Na_2B_4O_5(OH)_4 \cdot 8H_2O$ and $K_2B_4O_5(OH)_4 \cdot 2H_2O$, respectively.

Density of the System. The density data are plotted in Figure 4. The density increases with an increase of the potassium ion content at univariant curves except for curve DF_1. At the commensurate invariant point F_3, the system has the largest density.

Comparison with the Metastable and Stable Phase Diagrams. The stable phase diagram of the quaternary system $Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ has also been studied at (288[14] and 298) K.[15] Compared with the two stable phase diagrams at different temperatures, it is easy to observe that the crystallization field of the salt $Na_2CO_3 \cdot 10H_2O$ is obviously larger at 298 K than at 288 K, whereas the crystallization field of the potassium and sodium double salt is smaller at 298 K than at 288 K.

A comparison between the metastable phase diagram at 273 K and the stable phase diagram at 288 K[14] shows that the salts in this system, including the double salt, have the same crystallization forms, which are $Na_2CO_3 \cdot 10H_2O$, $K_2CO_3 \cdot 3/2H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, $K_2B_4O_7 \cdot 4H_2O$, and $Na_2CO_3 \cdot K_2CO_3 \cdot 12H_2O$ ($NaKCO_3 \cdot 6H_2O$). But, the crystallization fields of the salts have changed. The crystallization field of salt $Na_2B_4O_7 \cdot 10H_2O$ becomes larger with the temperature decrease, whereas that of the double salt $Na_2CO_3 \cdot K_2CO_3 \cdot 12H_2O$ becomes smaller, while the crystallization fields of the other salts change slightly. The results also show that, at low temperatures (273 K), the sodium borate is preferentially separated than the potassium borate at natural evaporation. If more borate needs to be separated as $K_2B_4O_7 \cdot 4H_2O$ as much as possible, a temperature rise is necessary.

Conclusion

The phase diagram and density of solution of the system $Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ were studied at 273.15 K. The isothermal evaporation method was employed. This system is of a complex type. In this system at 273.15 K, the double salt of sodium and potassium carbonate is formed with the form $K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$. The crystalloid forms of the other single salts are $Na_2CO_3 \cdot 10H_2O$, $K_2CO_3 \cdot 3/2H_2O$, $K_2B_4O_7 \cdot 4H_2O$, and $Na_2B_4O_7 \cdot 10H_2O$. $Na_2CO_3 \cdot 10H_2O$ is the only crystalloid form of sodium carbonate at 273.15 K, and $K_2CO_3 \cdot 3/2H_2O$ is the only crystallization form of potassium carbonate. The crystalloid forms of sodium borate and potassium borate exist with tetraborate, with the structure formed as $Na_2B_4O_5(OH)_4 \cdot 8H_2O$ and $K_2B_4O_5(OH)_4 \cdot 2H_2O$, respectively. Sodium borate has the largest crystallization field and can be easily separated from the solution in this system at 273.15 K using a crystallization method.

Literature Cited

(1) Zheng, M. P.; Liu, W. G.; Xiang, J. *Qinghai-Xizhang Plateau Saline Lakes* (in Chinese); Beijing Science and Technology Press: Beijing, China, 1989; pp 192−270.

(2) Shu, Y. G.; Li, J.; Jiang, C. F. Studies on the Metastable Phase Equilibrium of Na^+, K^+, Mg^{2+}/Cl^-, SO_4^{2-}-H_2O Quinary System at 288 K. *J. Chem. Ind. Eng. (China, Chin. Ed.)* **1992**, *43*, 549–555.

(3) Jin, Z. M.; Zhou, H. N.; Wang, L. S. Studies on the Metastable Phase Equilibrium of Na^+, K^+, Mg^{2+}/Cl^-, SO_4^{2-}-H_2O Quinary System at 288 K. *Chem. J. Chin. Univ.* **2002**, *23*, 690–694 (in Chinese).

(4) Jin, Z. M.; Xiao, X. Z.; Liang, S. M. Study of the Metastable Equilibrium for Pentanary System of (Na^+, K^+, Mg^{2+}), (Cl^-, SO_4^{2-}), H_2O. *Acta Chim. Sin.* **1980**, *38*, 313–321 (in Chinese).

(5) Jin, Z. M.; Zhou, H. N.; Wang, L. S. Studies on the Metastable Phase Equilibrium of (Na^+, K^+, Mg^{2+}), (Cl^-, SO_4^{2-}), H_2O Quinary System at 308.15 K. *Chem. J. Chin. Univ.* **2001**, *22*, 634–638 (in Chinese).

(6) Teeple, J. E. *The Industrial Development of Searles Lake Brines*; American Chemical Society monograph series: Washington, DC, 1928.

(7) Zeng, Y.; Lin, X. F.; Ni, S. J.; Zhang, C. J. Study on the Metastable Equilibria of the Salt Lake Brine System $Li_2SO_4 + Na_2SO_4 + K_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + K_2B_4O_7 + H_2O$ at 288 K. *J. Chem. Eng. Data* **2007**, *52*, 164–167.

(8) Zeng, Y.; Shao, M. Liquid-Solid Metastable Equilibria in the Quinary System $Li^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at $T = 288$ K. *J. Chem. Eng. Data* **2006**, *51*, 219–222.

(9) Xu, G. L. The Determination and Application of the Temperature Correction Coefficient for the Density of Vinyl Acetate. *Fujian Anal. Test.* **1999**, *3*, 1104–1108.

(10) Institute of Qinghai Salt-Lake of Chinese Academy of Sciences. *Analytical Methods of Brines and Salts*, 2nd ed.; Chinese Science Press: Beijing, 1984; pp 75−80.

(11) Zeng, Y.; Zheng, Z. Y. Phase Equilibria for the Aqueous System Containing Sodium, Potassium, Carbonate and Sulfate Ions at 273.15 K. *J. Chem. Eng. Data* **2009**, *54*, 1244–1248.

(12) Farmer J. B. Metal borates. In *Advances in Inorganic Chemistry and Radiochemistry*; Emeleus, H. J., Sharpe, A. G., Eds.; Academic Press: New York, 1982; Vol. 25.

(13) Li, J.; Gao, S. Y. Chemistry of borate. *J. Salt Lake Sci.* **1993**, *3*, 62–66 (in Chinese).

(14) Sang, S. H.; Yin, H. A.; Tang, M. L.; Zeng, Y. (Liquid + Solid) Phase Equilibria in the Quaternary System $Na_2CO_3 + K_2B_4O_7 + K_2CO_3 + Na_2B_4O_7 + H_2O$ at 288 K. *J. Chem. Eng. Data* **2004**, *49*, 1775–1777.

(15) Zeng, Y.; Yin, H. A.; Tang, M. L. A study on Phase Equilibrium of the Quaternary System Na^+, K^+/CO_3^{2-}, $B_4O_7^{2-}$ - H_2O at 298 K. *Chin. J. Inorg. Chem.* **2001**, *17*, 665–668.

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